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POLYAZIDOESTERS AS ENERGETIC POLYMERS AND COPOLYMER
COMPONENTS WITH FLUOR (U) ILLINOIS UNIV AT CHICAGO
CIRCLE DEPT OF CHEMISTRY R M MORIARTY 13 APR 88

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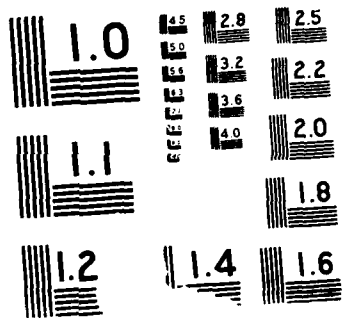
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POLYAZIDOESTERS AS ENERGETIC POLYMERS AND COPOLYMER COMPONENTS WITH
FLUORO DERIVATIVES

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April 13, 1988

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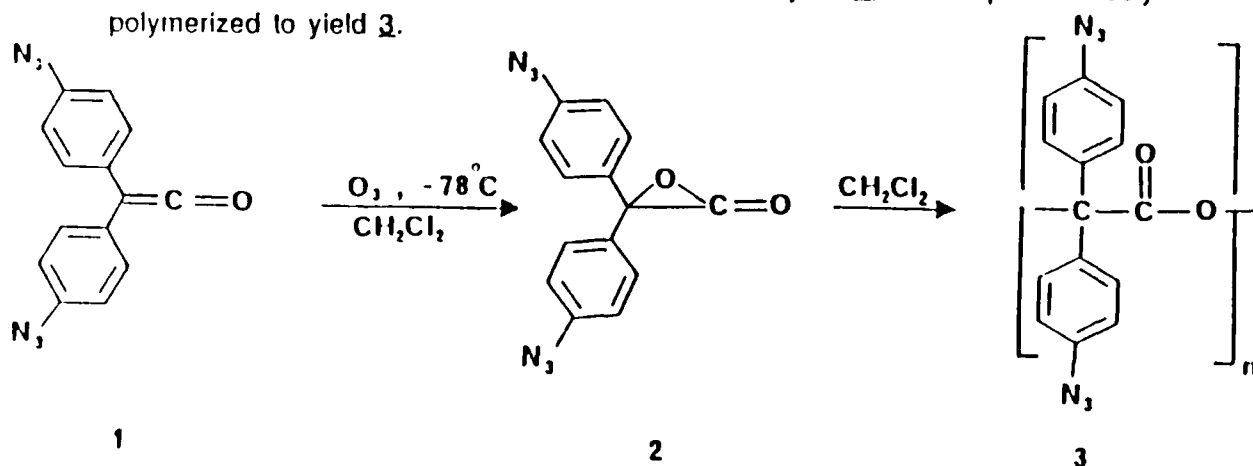
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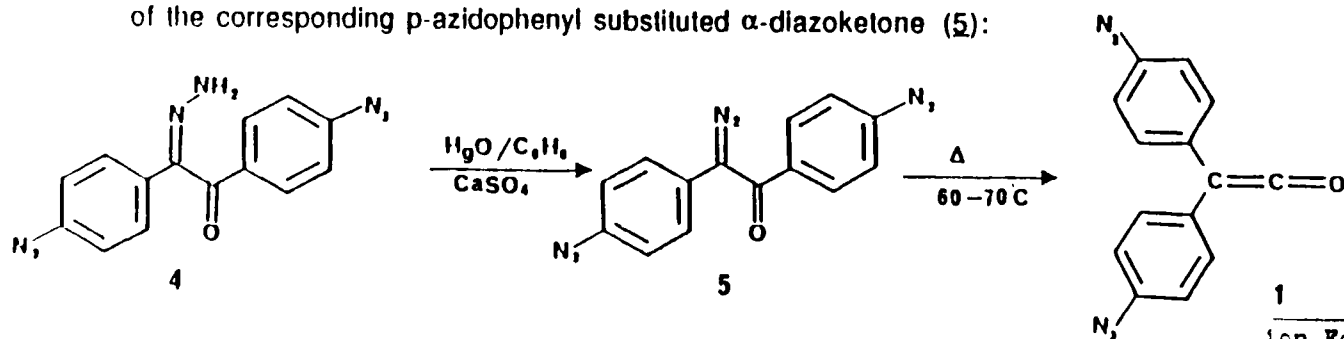
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Results

A primary objective of this program has been the synthesis of polyazidopolyesters. The approach used has been formation of an azidoketene which was subjected to ozonolysis to yield an intermediary α -lactone, which may be considered to be an unstable intermediate which undergoes polymerization. Specifically 4,4'-diazidodiphenylketene (1) was ozonized at -78°C to yield 2, which spontaneously polymerized to yield 3.



4,4'-Diazidodiphenylketene (1) was prepared by thermal or catalytic decomposition of the corresponding p-azidophenyl substituted α -diazoketone (5):



Compound 4 was synthesized starting via the benzoin condensation of 4-acetamidobenzaldehyde (6), which resulted in a satisfactory yield (42%) of the corresponding 4,4'-bis(acetylamino) benzoin (7)¹⁻³. Oxidation of (7) with copper sulfate in pyridine and water gave a 70% yield of 4,4'-bis(acetylamino)benzil (8).^{3,4} This compound was heated in a mixture of methanol and concentrated HCl until a yellow precipitate was formed⁵. After cooling and filtration, it was dissolved in water and aqueous ammonia was added in order to precipitate the expected 4,4'-diaminobenzil (9).



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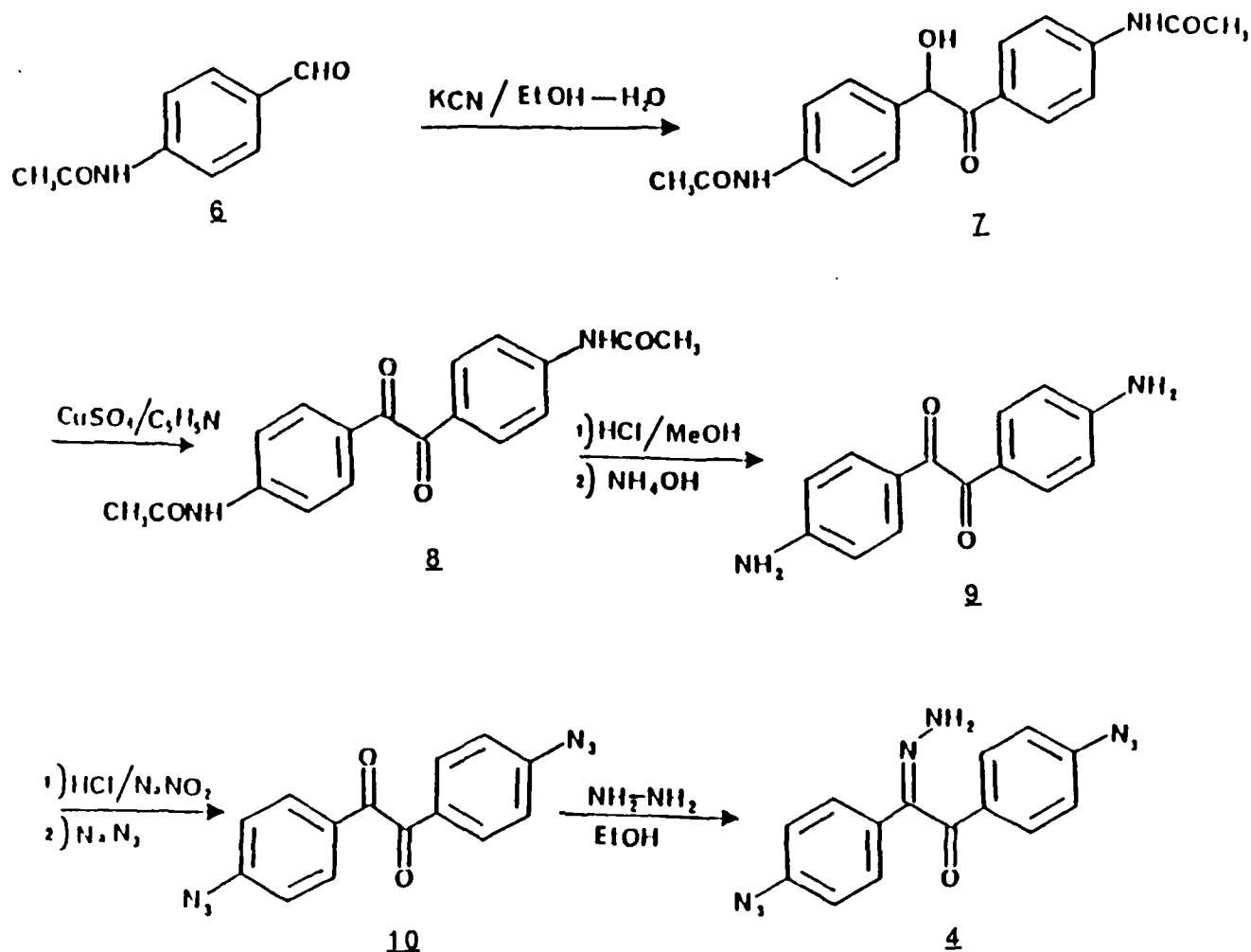
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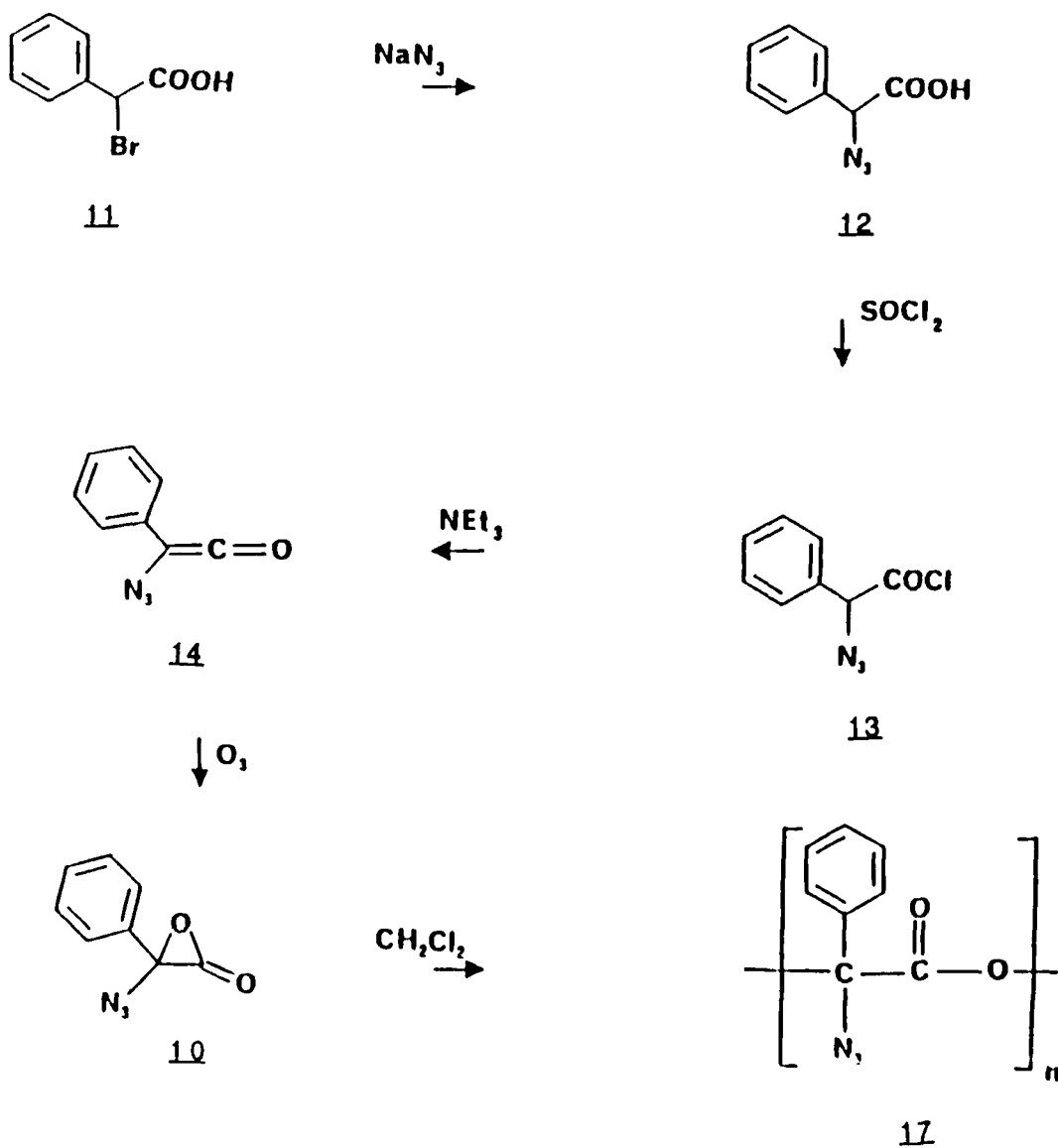
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After reprecipitation from hot ethanol and pentane (1:5 respectively) **9** was diazotized with sodium nitrite in HCl solution.⁶ The precipitated 4,4'-diazidobenzil (**10**) was collected by filtration and washed with cold water, then dried under vacuum to afford a yield of 67%. A hot ethanol solution of 4,4'-diazidobenzil (**10**) was treated with an equivalent of hydrazine (95%) under nitrogen gas. The reaction mixture was heated for another 5 minutes and then cooled to 0°C . The product (**4**) was collected, washed twice with cold (0°C) ethanol and dried in vacuum; yield 55%. Oxidation of 4,4'-diazidobenzil monohydrazone (**4**) was carried out using freshly prepared yellow mercuric oxide in dry benzene in the presence of anhydrous calcium sulfate to yield the expected 4,4'-diazidodiphenylketene (**1**) presumably *via* decomposition of the 4,4'-diazidodiazocompound (**5**). The procedure of Smith and Hoehn⁷ was used with the following differences. The reaction mixture was stirred for two days vigorously at $45\text{--}55^\circ\text{C}$. The yield of ketene as an oil is low (38%) and is best to be stored under nitrogen at low temperature. IR (neat): 2100 (N_3), 2090 ($\text{C}=\text{C}=\text{O}$) 1780, 1730, 1660, 1600 ($\text{C}=\text{C}$), 1500, 1290, 1220, 1170, 1035 and 1000 cm^{-1} . 4,4'-Diazidodiphenylketene

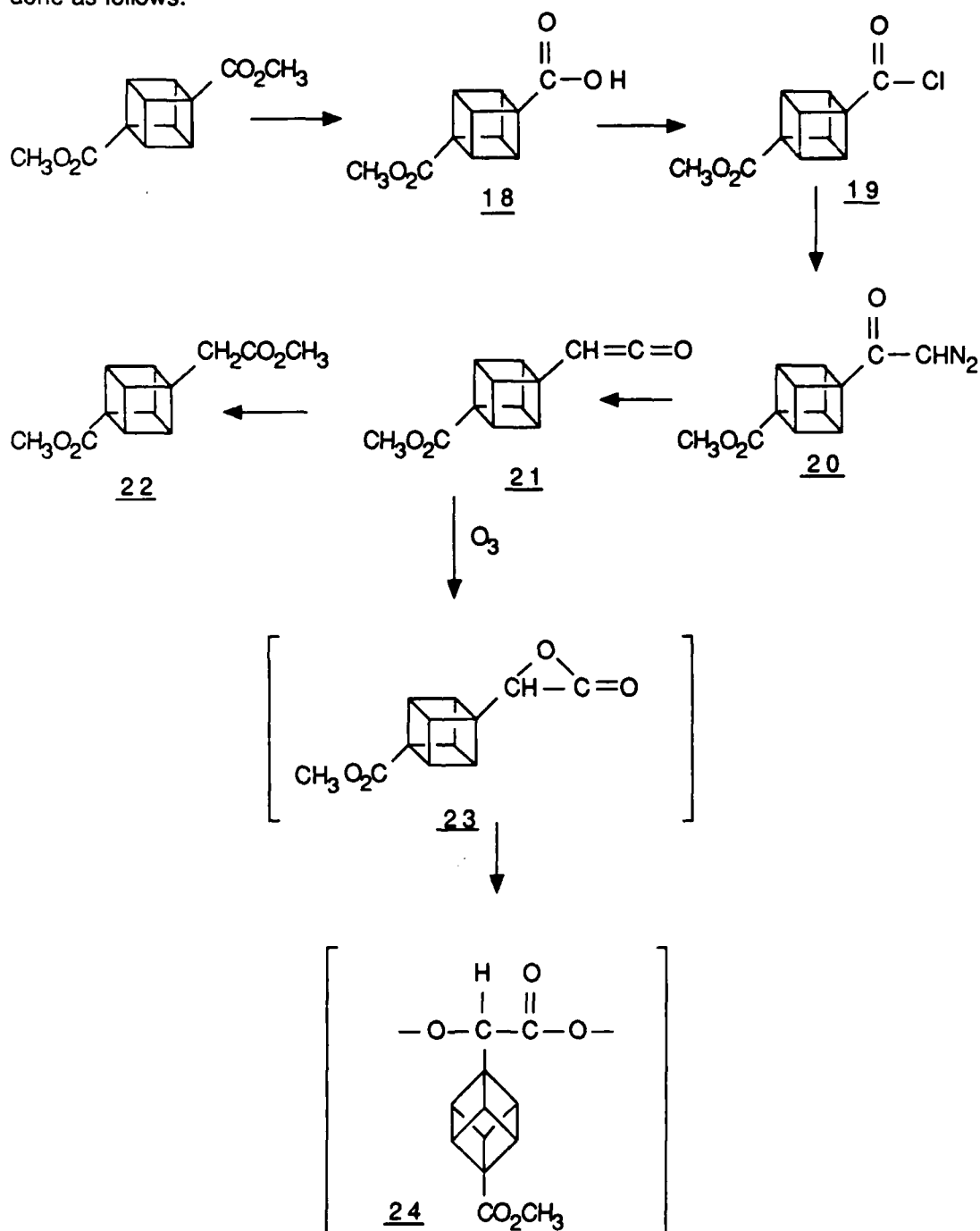
(1) was dissolved in dried dichloromethane in a sealed three neck flask and was ozonized at -78°C by bubbling ozone into the solution for 20 minutes. The solution became turbid and an insoluble precipitate appeared. The solution temperature was brought to room temperature and the solvent was concentrated and filtered. The precipitate as 4,4'-diazidophenyl polyester (3) was washed several times with pentane and dried in vacuum, yield 40%; IR(Nujol): 2100 ($-\text{N}_3$), 1740 ($-\text{CO}-\text{O}-$), 1600 ($\text{C}=\text{C}$), 1380, 1300, and 850 cm^{-1} .

The monoazido analog 15 was likewise synthesized via $11 \rightarrow 12 \rightarrow 13 \rightarrow 14 \rightarrow 15$. The intermediary 15 was not characterized but it underwent spontaneous polymerization to yield 17.



Polyazido Cubane Backbone Polymers

The first goal of this work was to synthesize the cubyl ketene analog 21. This was done as follows.



Next we undertook the synthesis of **25** which could be transformed in a similar fashion to a cubyl polyazido polymer.

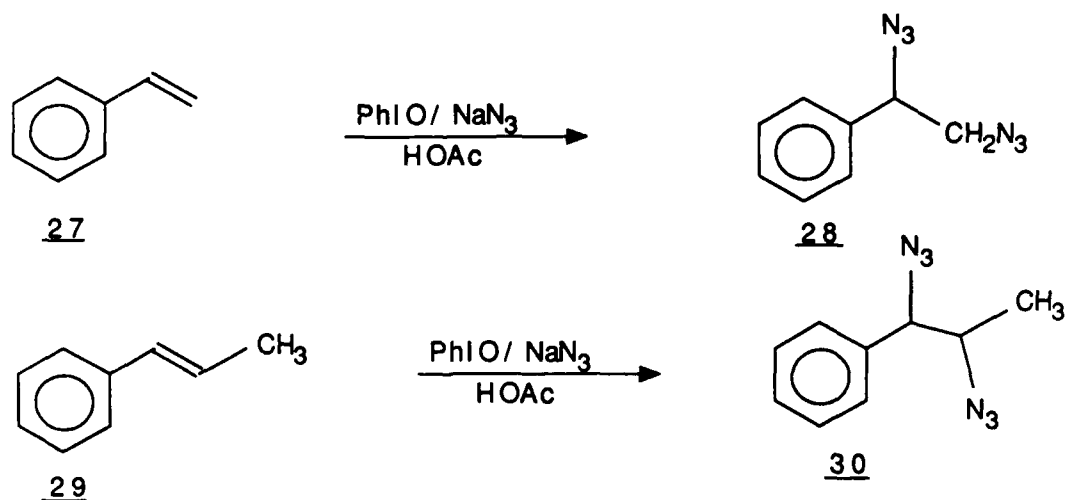
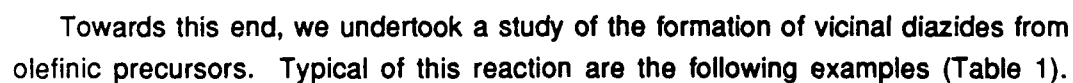
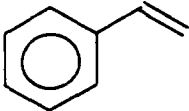
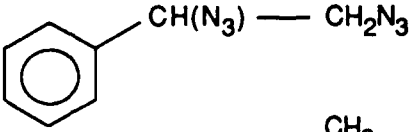
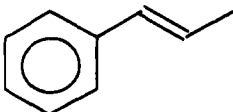
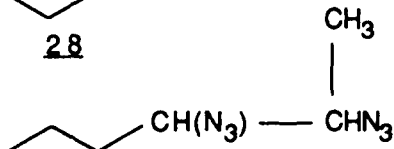
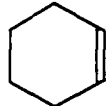
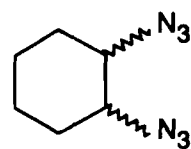
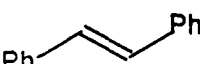
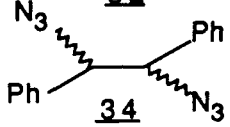
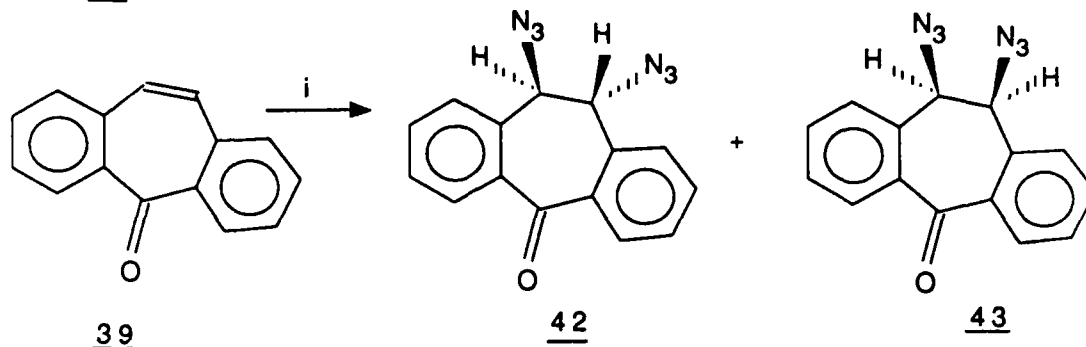
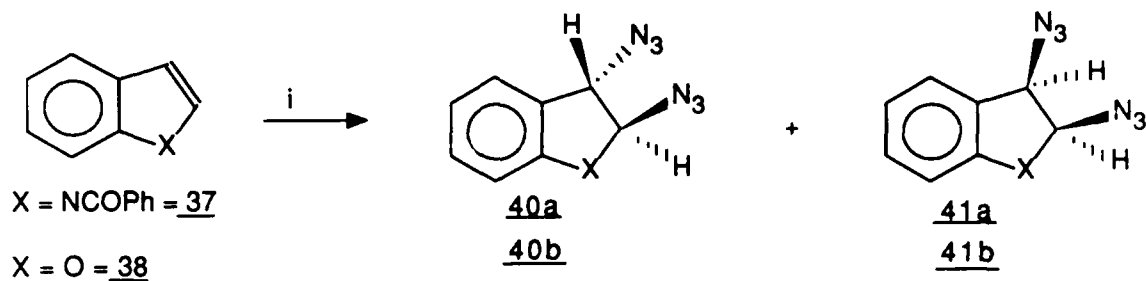


TABLE 1

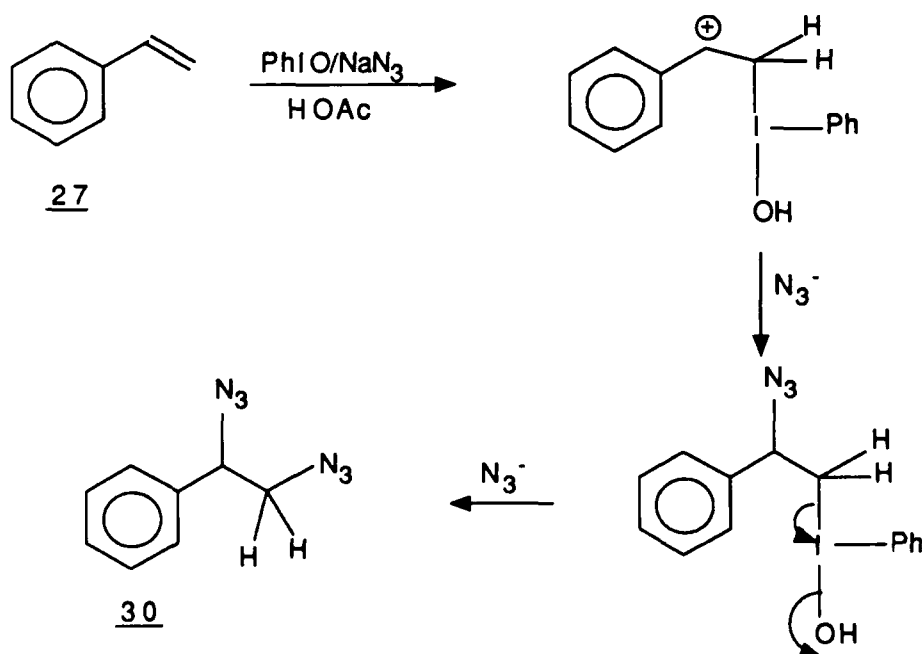
Alkene	Products	
 <u>27</u>	 <u>28</u>	70%
 <u>29</u>	 <u>30</u>	69%
 <u>31</u>	 <u>32</u>	40%
 <u>33</u>	 <u>34</u>	42%
N-benzoylindole (<u>37</u>) 45°, 3 hrs.	(34%) 40a:41b = 7:2	
benzofuran (<u>38</u>) R.T., 3 hrs.	(85%) 40a:41b = 7:3	
dibenzosuberone (<u>39</u>) 35°, 2 hrs.	(42%) 42:43 = 2:1	

Additional examples of this process use N-benzoylindole (37), benzofuran (38) and dibenzosuberone (39) with formation of the corresponding vincinal diazides.



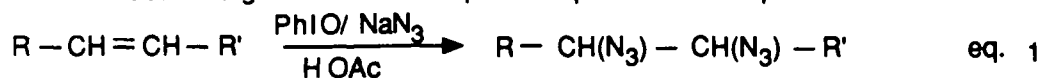
$i = \text{PhIO/HOAc/NaN}_3$

The mechanism by which these reactions occur involves the electrophilic $\text{C}_6\text{H}_5\text{I}^+\text{OH}$ which forms in situ and subsequently adds to alkenes. Then the generated azide anion in solution adds to the carbocation

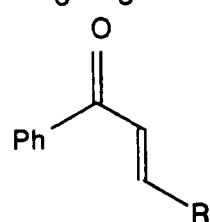


Reductive cleavage of carbon-iodine bond to form a carbocation (SN₁-like) or via displacement of HO⁻+I-C₆H₅ (SN₂-like) gives the corresponding vicinal diazide.

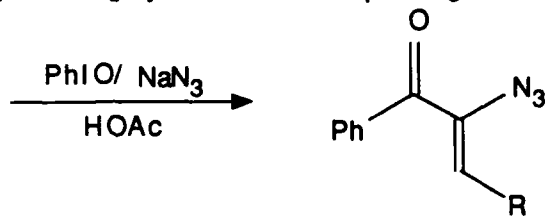
This reaction is general and examples are presented in eqn. 1.



We have found that chalcone (35) and benzalacetone (36) on reacting with PhIO/NaN₃/CH₃COOH gives a high yield of the corresponding α-azidovinyl ketone. (Table 2)



a = R = CH₃
b = R = C₆H₅

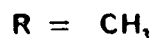
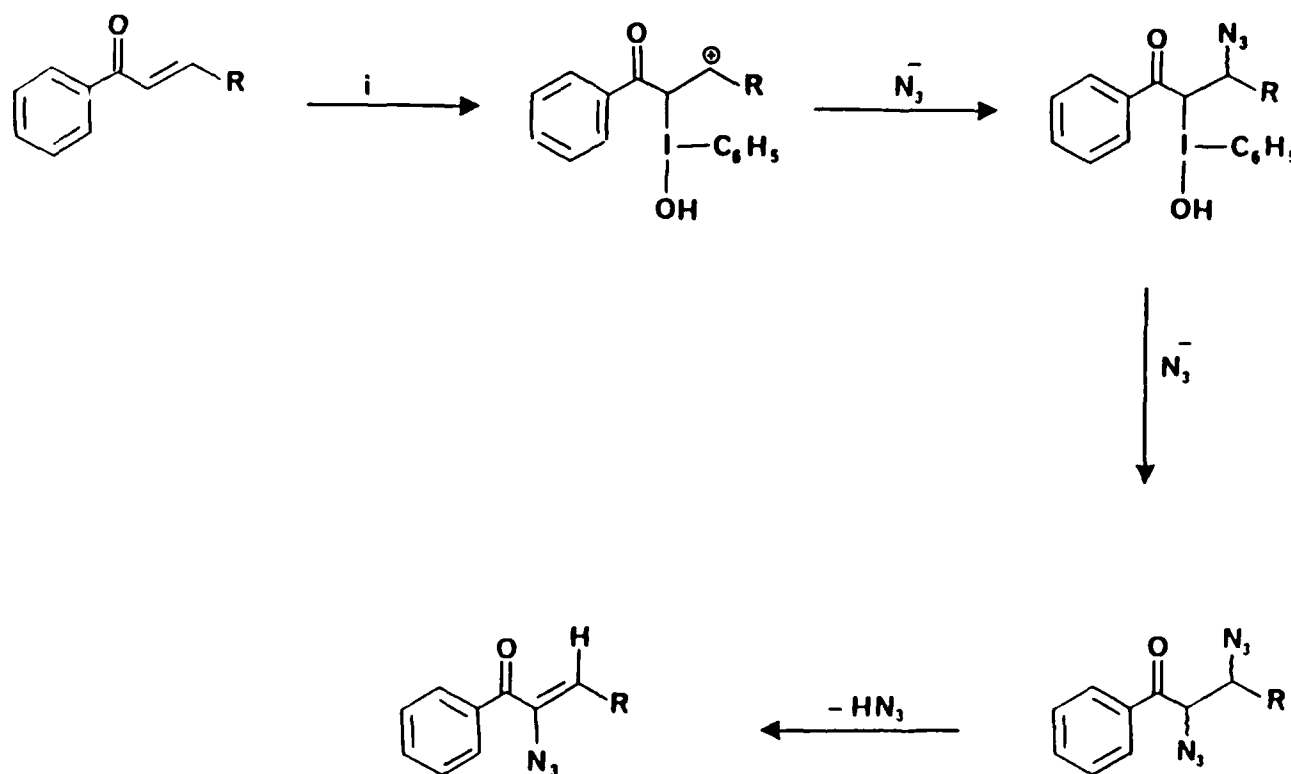


a = R = CH₃
b = R = C₆H₅

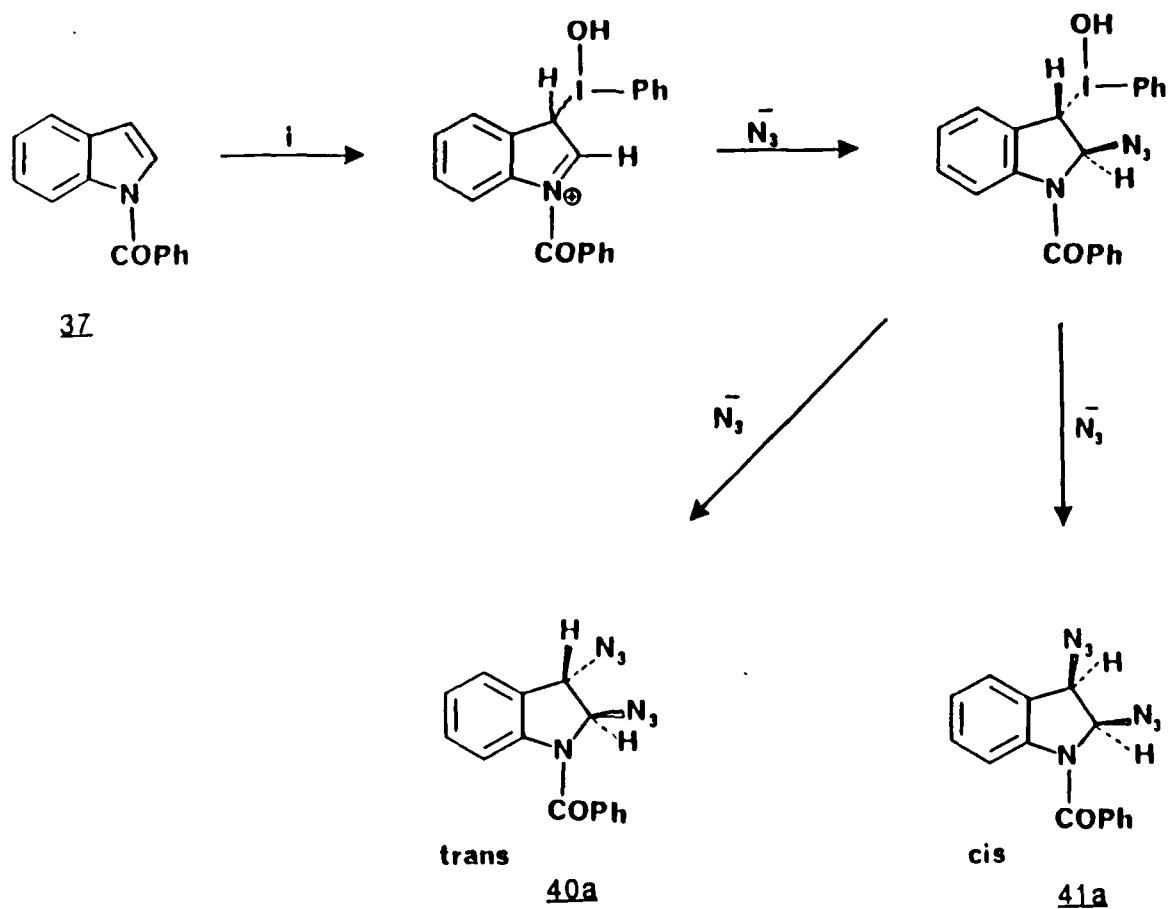
TABLE 2

Starting Material	Product	
		51%
		49%
		49%

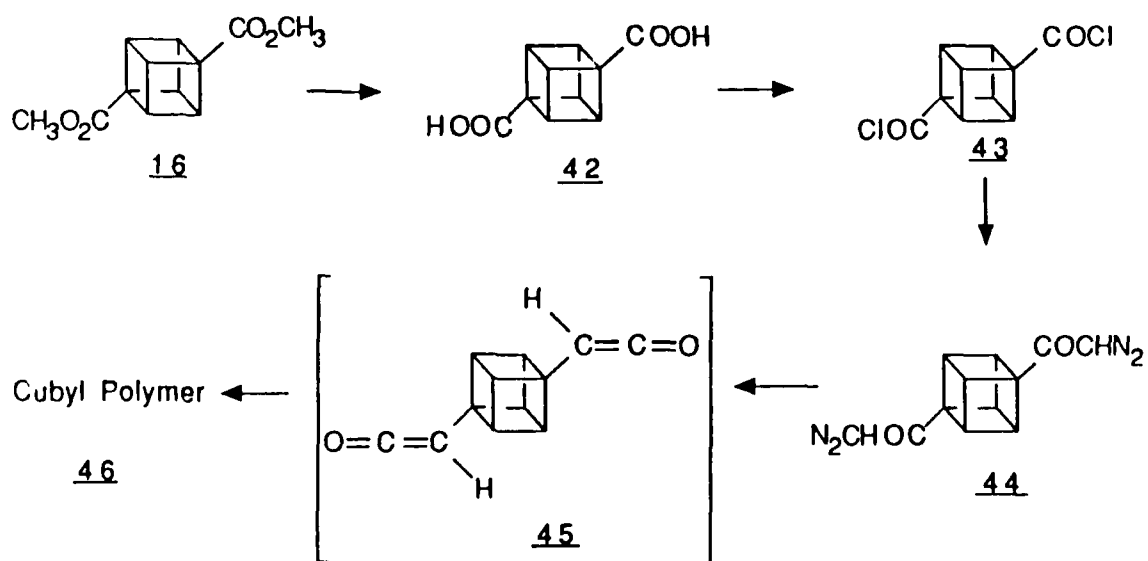
The formation of compounds 36, 36a, and 36b can be explained by initial addition of hypervalent iodine upon double bond or Michael type addition of azide anion. Then reductive cleavage of carbon-iodine bond either $\text{S}_{\text{N}}1$ -like or $\text{S}_{\text{N}}2$ -like mechanism followed by capture of azide anion to form the corresponding unstable vicinal diazide compound. The vicinal diazide loses hydrazoic acid to give the conjugated system α -azidovinyl ketone.



This mechanism applied to the case of *N*-benzoyl indole (37) might involve the following steps.



Synthesis of the cubyl diketene analog 45 was attempted by formation of 44 was unsuccessful.



Experimental

4,4'-Bis(acetylamino)benzoin (6)

Acetamidobenzaldehyde (1) (5.18 g, 0.032 mol) was added to a solution of potassium cyanide (400 mg, 0.06 mol) in 12 mL of 2:1 ethanol (8mL) - water (4 mL). The mixture was heated for 1 hour under reflux. In the course of about twenty minutes crystals of 4,4'-bis(acetylamino)benzoin (2) appeared. Refluxing was continued for another one hour, then the reaction was cooled to 0° C, filtered and washed with water (5 mL). The yield of crude benzoin (2) was 3.12 g (60%). After recrystallizing from hot 95% ethanol, pure 4,4'-bis(acetylamino)benzoin (6) was obtained (2.18 g, 42%); m.p. 241° C (Lit.³ m.p. 240-244° C); IR (Nujol) 3400-3100 (OH, NH), 1680 (C=O), 1600 (C=C), 1410, 1380, 1320, 1360, 1200, 1175, 1080, and 980 cm⁻¹; ¹H NMR δ : 8.00-7.2 (m, 8H), 5.95 (s, 1H), 2.1-2.2 (d, 6H).

4,4'-Bis(acetylamino)benzil (7)

A solution of cupric sulfate (10 g) in water (6 mL) and pyridine (20 mL) was heated until a clear solution was obtained. 4,4'-Bis(acetylamino)benzoin (6) (4.00 g, 0.012 mol) was added in small portions, the color of the solution changed from dark blue to dark green. After refluxing the mixture for 3 hours, the reaction mixture was poured into water (500 mL). The resulting crystalline precipitate was filtered and washed with water (100 mL). After recrystallizing ethyl acetate and pentane (1:5 respectively), 4,4'-bis(acetylamino)benzil (7) was obtained. It was dried in vacuo m.p. 239° C (Lit.³ m.p. 242° C); IR (Nujol): 3300 (NH), 1720, 1680 (C=O), 1600, 1590 (C=C), 1530, 1310, 12260, 1220, 1160, and 880 cm⁻¹; ¹H NMR δ : 7.9 (s, 8H), 2.2 (s, 6H).

4,4'-Diaminobenzil (8)

4,4'-Bis(acetylamino)benzil (7) (4.00 g, 0.012 mol) was added to a mixture of methanol (50 mL) and hydrochloric acid (concentrated, 15 mL). The mixture was heated until a precipitate formed. The reaction mixture was cooled to room temperature and filtered in vacuum. The yellow product was dissolved in water (50 mL) and treated with ammonium hydroxide solution (28-30%, 15 mL). It was recrystallized from hot ethanol and pentane (1:5 respectively). Yield 2.5 g, 68%; m.p. 166° C (Lit.³ m.p. 169° C); IR (Nujol): 3480 (NH₂), 3320 (NH₂), 1640 (C=O), 1590 (C=O), 1580, 1370, 1330, 1240, 1160 and 880 cm⁻¹; ¹H NMR (DMSO-d₆) δ : 7.5, 7.4, 6.7, 6.6

(g, 8H) aromatic; mass spectrum: m/e 222 (M^+ , 12%), 264 ($M^+ - N_2$), 236 ($M^+ - 2 \times N_2$), 208, 147, 146 (base peak, 100, $N_3 - C_6H_4 - CO^+$) 118 ($N_3 - C_6H_4 - CO^+ - (CO)$, 74%), 90 (base peak - (CO) , $-N_2$) and 39.

4,4'-Diazidobenzil Monohydrazone (4)

To a hot solution of 4,4'-diazidobenzil (8) (2.33 g, 0.008 mol) in ethanol (20 mL) was added an equimolar amount of hydrazine (95%, 30 μ L, 0.008 mol) dropwise under nitrogen gas (caution). The reaction mixture was heated for another 5 minutes and then cooled to 0° C in an ice bath. 4,4'-Diazidobenzil monohydrazone (4) separated out of solution and was collected, washed with cold (0° C) ethanol and dried in vacuum, yield 1.32 g, 55%; m.p. 115° C, IR (Nujol): 3400, 3300 (NH_2), 3200, 2100 ($-N_3$), 1620 ($C=O$), 1600 ($C=C$), 1540, 1500, 1470, 1380, and 880 cm^{-1} ; 1H NMR (DMSO, $CDCl_3$) δ : 8.00, 7, (d, 2H), 7.6 (b, 2H), 7.3-7.0 (m, 6H); mass spectrum: m/e 306 ($M^+ - N_2$, 100%), 250 ($M^+ - 2 \times N_2$), 222 ($M^+ - 2 \times N_2 - CO$, 4%), 210, 195, 194, 182, 118 (12%).

4,4'-Diazidodiphenylketene (1)

4,4'-Diazidobenzil monohydrazone (4) (1.12 g, 0.004 mol) was mixed in a mortar with freshly prepared yellow mercuric oxide (3.24 g, 0.015 mol) and anhydrous calcium sulfate (1.4 g, 0.01 mol). The mixture was introduced into a three necked flask equipped with a mechanical stirrer, condenser and a thermometer. Thiophene-free dry benzene (25 mL) was added and the mixture stirred vigorously at 45° C for two days; the mixture was then filtered and washed with dry benzene (20 mL). The benzene solution of diazidodiazocompound (5) was stirred for another 2 hours at 62°-70° C, and then the benzene was removed *in vacuo*. The residue as an oil was found to be 4,4'-diazidodiphenylketene (1), oil, yield 0.37 g, 38%; IR (neat): 2100 ($-N_3$), 2090 ($C=C=O$), 1780, 1730, 1660, 1600 ($C=C$), 1500, 1290, 1220, 1170, 1035 and 1000 cm^{-1} . It was stored under nitrogen gas at low temperature in order to avoid polymerization.⁸

4,4'-Diazidodiphenyl Polyester (3)

The freshly prepared 4,4'-diazidodiphenylketene (1) (0.36 g, 0.001 mol) was dissolved in dried dichloromethane (20 mL) under nitrogen gas in a sealed three necked flask. The flask was cooled to -78° C in dry ice/acetone, then ozone was introduced into the solution for 20 minutes with vigorous stirring. The solution became turbid and a precipitate appeared. The solution was brought to room temperature, the solvent was concentrated, a few drops of pentane were added, and finally, the product was filtered and

washed with pentane (25 mL). The product, 4,4'-diazidophenyl polyester (**3**), (0.152 g, 40%) was collected. Solid, IR (Nujol): 2100 (-N_3), 1740 (-COO-), 1600 (C=C), 1300, and 850 cm^{-1} . In order to interpret the observed spectra of azide compounds, comparison with diphenylketene (oil) was necessary. IR (neat): 2090 (C=C=O), 1810, 1750, 1670, 1600 (C=C), 1500, 1540, 1290, 1280, 1170, 1070, and 1030 cm^{-1} and diphenylpolyester (solid, yield 46%); IR (Nujol) 1755 (-CO-O-), 1600 (C=C), 1260, 1170, and 1090 cm^{-1} yield 2.8 g, 70%).

Pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane-1,4-dicarboxylic Acid Dimethylester (**16**).

Available in multigram scale according to the procedure of Eaton, P. E. et. al.⁹

Pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane 1,4-Dicarboxylic Acid Monomethyl Ester (**18**).

The above was prepared by half-saponification of the corresponding dimethyl ester in the following manner: to a solution of cubyl 1,4-dimethyl ester (5.6 g, 25.45 mmol) in [ether (210 mL) + tetrahydrofuran (130 mL)] was added a solution of sodium hydroxide (1.074 g, 26.85 mmol) in hot methanol (29 mL). Upon addition of the sodium hydroxide solution, the reaction mixture turned pale yellow, after which some precipitate was formed. The mixture was stirred overnight at room temperature. The reaction mixture was then concentrated under reduced pressure, dissolved in water (150 mL) and extracted with CuCl_3 (2 X 60 mL). [After drying (MgSO_4), the chloroform layer gave a 2% yield of starting material.] The aqueous layer was carefully acidified with hydrochloric acid to a pH of 3, after which the desired product (cubyl-1,4-dicarboxylic acid monomethyl ester) precipitated easily, and this was collected by filtration (3.250 g, 62%). The filtrate was extracted with chloroform (4 X 80 mL), dried (MgSO_4), and removed under reduced pressure, giving the second crop of monomethyl monoacid (1.018 g, 12.5%). The aqueous layer was further acidified to pH < 2 by the addition of concentrated hydrochloric acid. Sodium chloride was added until the mixture was saturated; it was then extracted with ethyl acetate (3 X 50 mL), dried (MgSO_4), and the ethyl acetate was removed under reduced pressure, giving 72 mg of fully hydrolyzed cubane 1,4-dicarboxylic acid.

Pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane-1-carboxylic Acid Methylester-4-carboxylic Acid Chloride (**19**)

Freshly prepared cubyl-1,4-dicarboxylic acid monomethyl ester (1.3 g, 5 mmol) was refluxed in thionyl chloride (35 mL). The resulting yellow solution was stirred and refluxed for 6 hours. The excess thionyl chloride was removed under reduced pressure to give a quantitative yield of the desired acid chloride. M.p. $95^\circ\text{-}97^\circ\text{ C}$. IR (Nujol): 1790 (COCl), 1730 (COOCH_3).

Pentacyclo [4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane-1-carboxylic Acid Methylester-4-diazoketone (20).

1 G of pentacyclo [4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane-1-carboxylic acid methylester -4-carboxylic acid chloride, 2g, was dissolved in 200 mL of Et₂O and titrated with a dilute solution of diazomethane in Et₂O to disperse the yellow color. The Et₂O solution was washed with ice water, dried, and concentrated to yield the diazoketone.

Pentacyclo [4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane-1-carboxylic Acid Methylester -4-ketene (21).

1.5 G of the above diazoketone was stirred at reflux in 100 mL of dry Et₂O with 150 mg Rh₂(OAc)₄ for 48 hrs. At the end of this time, the solution was filtered, dried and concentrated to dryness *in vacuo*. The crude product, 1.2 g showed typical ketene absorption in the IR, 1785, 1732 cm⁻¹. A sample, 100 mL, was refluxed in methanol for 12 hours to yield the corresponding diester. The crude ketene was ozonized as above at -78° C in dry CH₂Cl₂ for 15 min. Concentration of the solvent to dryness *in vacuo* yielded the polyester(24) in 85% yield.

Pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane-1,4-dicarboxylic acid (42).

The above was prepared by saponification of dimethyl ester (16). Pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]octane-1,4-dimethyl ester (16) was added to a solution of sodium hydroxide (NaOH) (1.76, 22 mmol) in methanol (70 mL). Upon addition of the cubyl diester, the mixture turned pale yellow. Another 30 mL of methanol was added, and stirred for 30 minutes, after which the mixture was refluxed overnight. The reaction mixture was cooled to room temperature and methanol was removed under reduced pressure. The residue was dissolved in water (70 mL), extracted with a small amount of chloroform and saved. The aqueous layer was acidified with 2N HCl. At this time, the 1,4-cubyl diacid was precipitated and collected by filtration (2.5 g, 66%). A second crop was obtained as follows: the aqueous layer was saturated with ammonium chloride and extracted with tetrahydrofuran, dried (MgSO₄), and evaporated under reduced pressure to give 2 (440 mg, 11.5%). Total 77.5%, m.p. 228-230° C.

Pentacyclo [4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane-1,4-dicarboxylic Acid Chloride (43)

Freshly prepared cubyl 1,4-dicarboxylic acid (1.7 g) was refluxed in thionyl chloride (80 mL). After the acid went into solution, it was then refluxed for 4 hours. Excess thionyl chloride was distilled off and the residue found was pure acid chloride. IR (Nujol): 1730 cm⁻¹ (COCl).

1,2-Diazidodiphenylethane (34)

To a solution of iodosobenzene (2.2 g, 0.01 mol) in acetic acid (30 mL) was added trans-stilbene (33) (1.8 g, 0.01 mol) after 20 minutes sodium azide (2.6 g, 0.04 mol) was added behind safety shield and the reaction was kept stirring at 50° C for 2 hours, then cooled to room temperature and poured into water (100 mL), extracted with chloroform (2 X 100 mL), dried over MgSO₄ and evaporated to give 1.1g, (42%) mixture of d,l and meso 1,2-diazidodiphenylethane (34). m.p. 95° C, IR (Nujol), 3010, 2100 (N₃, very strong) cm⁻¹; ¹H NMR δ: 4.57, 4.62, (d, 2H), 7.1-7.7 (m, 10H).

2-Azido-1.3-diphenyl-1-propene-3-one (36a)

To a solution of iodosobenzene (2.2 g, 0.01 mol) in acetic acid (30 mL) was added chalcone (35e) (2.08g, 0.01 mol) after stirring for 20 minutes at room temperature sodium azide (2.6 g, 0.04 mol) was added portion by portion behind a safety shield. The reaction mixture was stirred for 3.5 hours at 40° C, then poured into water (150 mL) and extracted with chloroform (2 X 100 mL). The combined extracts were dried over MgSO₄ and evaporated under reduced pressure gave (1.26 g, 51%) of the above compound (36a). m.p. 64-65° C (lit. m.p. 63.5-64° C); IR(Nujol) 3010, 2100 (N₃ very strong), 1700 (C=O) cm⁻¹; ¹H NMR δ: 6.47 (s, 1H), 7.25-7.9 (m, 10 H).

α-Azidobenzylideneacetone (36b)

To a solution of iodosobenzene (2.2 g, 0.01 mol) in acetic acid (25 mL) was added trans-4-phenyl-3-buten-2-one (35b) (1.45 g, 0.01 mol) and stirred for ten minutes, then sodium azide (2.6 g, 0.04 mol) was added. The reaction mixture stirred for 2.5 hours at 45° C, then the work up was followed to give (0.91 g, 49%) yield of crystalline compound (36b) m.p. 75-76° (lit. m.l.p. 79-80° C); IR (Nujol) 3000, 2100 (N₃, very strong) 1680 (C=O) cm⁻¹; ¹H NMR δ: 2.42 (s, 3H), 6.65 (s, 1H), 7.25-8.00 (m, 5H).

1,2-Diazido-1-Phenylethane (28)

Iodosobenzene (2.2 g, 0.01 mol) was dissolved in acetic acid (28 mL), to this solution was added styrene (27) (1.14 mL, 0.01 mol). After stirring for 30 minutes, sodium azide (2.6 g, 0.04 mol) was added behind safety shield. The reaction mix was stirred at 35° C for 3 hours then poured into water (100 mL) and extracted with chloroform (2 X 75 mL). The chloroform solution dried over MgSO₄ and evaporated under reduced pressure to give 1.31 g (70%) of the corresponding 1,2-diazido-1-phenylethane (28) as a pale yellow oil, IR (liquid film) 3050, 2940 (CH), 2100 (N₃

very strong) cm^{-1} ; $^1\text{H-NMR}$ δ : 3.40 (d, 2H), 4.65 (t, 1H), 7.35 (s, 5H).

1,2-Diazo-1-phenylpropane (30)

Compound 30 was prepared from the reaction of 1.30 mL (0.01 mol) of trans- β -methylstyrene (29), iodosobenzene (2.2 g, 0.01 mol) in acetic acid (30 mL) with sodium azide (2.6 g, 0.04 mol). The reaction mixture was stirred at 45°C for 2.5 hours, then poured into water (100 mL) and extracted with chloroform, dried (MgSO_4), evaporated under reduced pressure to give the above compound (30) (1.34 g, 69%) as an oil, IR (liquid film) 3000, 2940, 2100 (N_3 very strong) cm^{-1} . ^1H NMR δ : 0.9-1.4 (m, 3H), 3.2-3.9 (m, 2H), 4.3-4.5 (d, 1H), 7.35 (s, 5H).

1,2-Diazidocyclohexane (32)

To a solution of cyclohexene (31) (1.01 mL, 0.01 mol) in acetic acid (30 mL) was added iodosobenzene (2.2 g, 0.01 mol), after stirring for 10 minutes sodium azide (2.6 g, 0.04 mol) was added and the reaction mixture was kept at 45°C for 3 hours, then was poured into water and extracted with chloroform, dried (MgSO_4), evaporated and chromatographed on silica gel to give 0.66 g (40%) of clean oil IR (liquid film), 2950, 2870, 2100 (N_3 , very strong) cm^{-1} ; ^1H NMR δ : 3.3-3.7 (m, 2H), 0.9-2.2 (m, 8H).

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